THE INITIATION OF HOT-SALT STRESS CORROSION CRACKING OF TITANIUM ALLOYS*

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ABSTRACT

The initial stages of hot-salt stress corrosion cracking of titanium alloys were studied using hot-stage microscopy and cinematography. An incubation period for cracking was observed, the duration of which depends on exposure temperature, salt composition, and alloy composition. For Ti-8Al-1Mo-1V exposed to NaCl the incubation period decreased from about 96 hours at 475°F, to 20 hours at 500°F, to 1-1/2 hours at 650°F, to only 10 minutes at 850°F. This same alloy cracked severely in only 20 minutes at 475°F when exposed to $SnCl_2$, indicating that the apparent "threshold temperature" for cracking is strongly influenced by chemical environment. At 650°F the incubation period for NaCl cracking of four alloys containing aluminum increased with decreasing aluminum content.

Cracks appeared abruptly and propagated rapidly for a short distance, then apparently paused for additional corrosion-embrittlement to occur. Moisture was demonstrated to be a vital ingredient in hot-salt attack and the presence of absorbed hydrogen in salt-corroded areas has been demonstrated using radiotracer H^3 (tritium). These results support the hypothesis that absorption of corrosion-produced hydrogen promotes embrittlement and crack initiation.

INTRODUCTION

Rapid advancements in the technology of titanium alloys have been made during the past five years, and there has been a sharp increase in the use of these alloys in the production of jet engines and airframes. A number of problems remain, however, that may hinder further increases in applications of titanium alloys. Among these problems, the phenomenon known as "hot-salt stress corrosion cracking" is of interest to the aircraft industry. This form of stress corrosion damage can occur when certain halide salts are present as surface contaminants on titanium alloys that are stressed and exposed to elevated temperatures. Fortunately, this phenomenon was first revealed by laboratory tests rather than by a rash of service failures. Some cases of cracking have occurred during fabrication heat treatments.[1] The threat of hot salt cracking in service is of great concern because salt contamination of aircraft is certain to occur in coastal airports.

Extensive laboratory investigations of hot-salt cracking have been performed, and the results of these were reviewed at a recent symposium.[2] Although much has been learned about the conditions under which cracking can occur, many aspects of the phenomenon are not adequately understood. For example, it has been reported that cyclic heating from room temperature to 550°F causes much less stress corrosion damage than continuous heating at 550°F.[3,4] This implies that some time at temperature is required for corrosion reactions to produce conditions that lead to cracking. It has been suggested that absorption of corrosion-produced hydrogen causes embrittlement, and radiotracer studies

have shown that hydrogen is present in salt-corroded areas of the metal.[5] Another suggestion is that some crack-promoting phase is generated by the salt reactions, and that this phase is converted to a harmless product during the cooling portions of cyclic exposures.[4] Various crack-promoting phases have been suggested, including liquid,[1] gaseous,[6] and solid.[7] The concept of a crack-promoting phase has also been advanced in connection with a hypothesis that there is a threshold temperature for hot-salt cracking which corresponds to the minimum temperature for formation of the critical phase. However, the minimum temperature for hot-salt cracking depends on several variables such as stress level and alloy composition,[8] and a specific threshold temperature has not be identified. Because of these and other uncertainties, the mechanism of hot-salt cracking has remained in doubt.

A program of research to develop fundamental knowledge about the mechanism of hot-salt cracking is in progress at the Savannah River Laboratory under the sponsorship of the National Aeronautics and Space Administration. This paper presents the results of a part of that program in which the initial stages of cracking were studied using hot-stage microscopy and cinematography. The specific objectives of these studies were to observe the nature of hot-salt attack on the metal surface, looking especially for any relationship between visible corrosion products and crack initiation, and to determine the effects of alloy composition and exposure temperature on the initiation of cracks. Several important features of the cracking process were revealed which help to explain the different

effects of cyclic versus static exposures. Also, additional evidence was obtained supporting a hypothesis advanced in a previous paper[5] that moisture is a critical ingredient in hot salt attack and that absorption of corrosion-produced hydrogen promotes cracking.

EXPERIMENTAL PROCEDURES

All specimens were strips 3/4" x 3 inch with metallographically polished surfaces. The specimens were stressed in four-point loading fixtures to a calculated fiber stress of 100,000 psi at room temperature, which caused them to yield slightly when heated to test temperatures. For experiments to determine the time to initiate cracking, deposits of sodium chloride were applied in the area of maximum stress by evaporating three drops of saturated aqueous solution on the specimens at room temperature. (A few tests were performed using other chloride salts, as indicated in the discussion.) This procedure produced a fairly dense deposit of coarse crystals covering a spot about 1/2 inch in diameter. Multiple specimens were then heated isothermally in stagnant air using a small electric oven. Specimens were removed at intervals, and after removing the salt deposits, the surfaces were microscopically examined for evidence of cracking.

In order to permit direct observation of salt reactions on specimens examined by hot-stage microscopy, droplets of a very dilute salt solution were evaporated on the pre-polished surfaces.

The resulting salt crystals were small enough to be viewed with
a conventional metallurgical microscope. Specimen heating was
accomplished by placing a tiny, hand-made coil of resistance
wire against the underside of the specimen and adjusting the
current with a powerstat. Asbestos cloth was used to insulate
the specimen loading fixture, which was positioned directly on
the microscope stage.

The temperature in the area of the salt deposit was measured
with a fine-wire thermocouple held in contact with the surface.
Although the temperature control was not precise, this simple
arrangement proved to be quite satisfactory, and the times
observed for initiation of cracking at any given temperature
agreed reasonably well with those determined by the isothermal
oven tests. Photomicrographs at magnifications up to 720X were
obtained with a 35 mm camera. Movies of the hot-salt stress cor-
rosion process were made through the microscope at magnifica-
tions up to 200X using a 16 mm camera equipped with a single
frame attachment for speeds down to one frame per second.

RESULTS AND DISCUSSION

Hot-Stage Microscopy of Ti-8Al-1Mo-1V

The relationship between corrosion and the initiation of
cracking by NaCl was studied first on specimens of Ti-8Al-1Mo-1V
at 650°F. The direct, hot-stage microscopic observations revealed
that corrosion stains began to develop within minutes after the
specimen surface reached 650°F, but cracking did not begin until
about 1-1/4 to 1-1/2 hours later.

Initially, the corrosion stains appeared as microscopic speckles that developed on the metal around the salt crystals. The number of speckles increased with time, Figure la,b,c, and gradually formed a fairly continuous stain around the salt. However, the stains did not appear to form by surface diffusion of reaction products spreading out from salt-metal contact areas, and the initiation of cracking occurred before the stain became continuous, Figure ld.

Cracks appeared abruptly, propagated rapidly for a short distance, and then apparently paused for additional corrosion-embrittlement to occur. Further propagation also appeared to occur by abrupt extensions. Although cracks always originated at points of salt contact, there was no apparent relationship between the size of the salt crystals and the size of the cracks. Many cracks were initiated at extremely small salt crystals. At various intervals after the first cracks appeared, additional cracks were initiated at other sites. In many cases, these sites were close together and the cracks connected to form larger cracks. An example of this is shown in Figure 2.
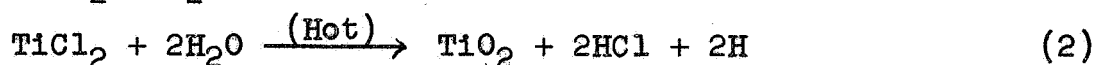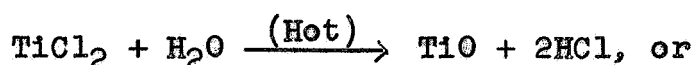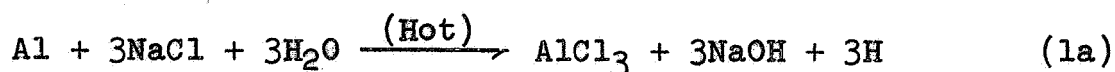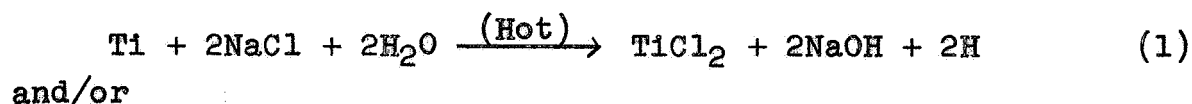
The speckled corrosion stain has not been identified, but it has been shown to be a very thin, non-adherent flaky substance which tends to spall off as the specimens cool to room temperature and which is completely removed by a water rinse. It was concluded that the speckled stain is produced by reactions with constituents (probably chloride ions and moisture) adsorbed on the specimen surface. In order to prove that the speckles were not produced by reactions with constituents in the air, specimens

that had not been wetted with salt water were heated with and without predried salt crystals on their surfaces. No corrosion stains were produced in either case, which indicated that adsorbed constituents caused the stains, and also demonstrated that moisture is a vital ingredient in the hot-salt corrosion process, Figure 3. Previous work[5] with radiotracer H[3] (tritium) in the solutions from which salt was deposited on specimens showed that hydrogen is absorbed in salt-corroded areas. The combined results of the radiotracer studies and hot-stage microscopic observations support the hypothesis that absorption of corrosion-produced hydrogen promotes crack initiation.
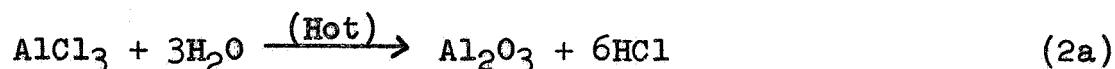
Effects of Temperature on Cracking of Ti-8Al-1Mo-1V by NaCl
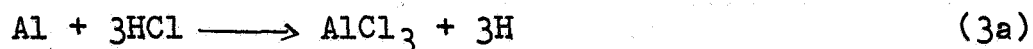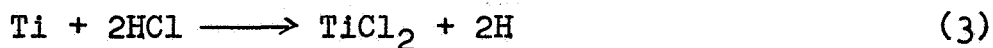
The effect of exposure temperature on the incubation period for crack initiation in Ti-8Al-1Mo-1V is shown in Figure 4. The incubation period decreased from about 96 hours at 475°F to 20 hours at 500°F to about 1 hours at 700°F. An obvious inflection occurred in the incubation-temperature curve between 700° and 750°F. From 750° to 950°F the incubation period decreased from about 45 minutes to only about 6 minutes. These results indicate two significant points for discussion: (1) the long incubation periods at the lower temperatures provide an explanation for previous reports that cyclic heating to 550°F caused less stress corrosion damage than continuous heating at the same temperature,[3,4] and (2) the inflection in the incubation time-temperature curve indicates a change in the salt stress corrosion process between 700° and 750°F.

During cyclic exposures in which the time at temperature is less than the incubation period, the initiation of cracking either will not occur or will require some number of cycles before sufficient corrosion-embrittlement occurs to produce cracking. Pride and Woodward[3] have demonstrated that increasing the time-at-temperature portion of cyclic exposures does increase the extent of damage in residually stressed specimens. Piper and Fager[4] used a 3-hour cycle between room and 500°F temperatures with rewetting in salt solutions after each cycle, and they reported no damage in dead-weight loaded tension specimens after a total time of 2000 hours. Their time-at-temperature during each cycle was 2-1/2 hours, which is considerably shorter than the incubation period (~10 hours) at 550°F shown in Figure 4. Piper and Fager[4] suggested that some detrimental corrosion product generated at 550°F might be washed off or converted to a harmless form during the room-temperature portion of their cycle. This is a definite possibility, especially if the corrosion reactions occur in the sequence previously suggested:[5]

$$Ti + 2NaCl + 2H_2O \xrightarrow{\text{(Hot)}} TiCl_2 + 2NaOH + 2H \qquad (1)$$

and/or

$$Al + 3NaCl + 3H_2O \xrightarrow{\text{(Hot)}} AlCl_3 + 3NaOH + 3H \qquad (1a)$$

$$TiCl_2 + H_2O \xrightarrow{\text{(Hot)}} TiO + 2HCl, \text{ or}$$

$$TiCl_2 + 2H_2O \xrightarrow{\text{(Hot)}} TiO_2 + 2HCl + 2H \qquad (2)$$

and/or

$$AlCl_3 + 3H_2O \xrightarrow{\text{(Hot)}} Al_2O_3 + 6HCl \qquad (2a)$$

$$Ti + 2HCl \longrightarrow TiCl_2 + 2H \qquad\qquad (3)$$

$$Al + 3HCl \longrightarrow AlCl_3 + 3H \qquad\qquad (3a)$$

(Repeat reactions 2, 2a, and 3, 3a.)
Cooling to room temperature and rewetting with salt solution
before significant progression of these reactions would
hydrolyze the initial corrosion products (metal chlorides)
and produce oxide phases which would tend to block further
reactions on reheating. This would also retard absorption of
corrosion-produced hydrogen and possibly prevent buildup to a
concentration that would promote further cracking.

The inflection in the incubation time-temperature curve
between 700° and $750^{\circ}F$ suggests the possible formation of either
a liquid or gaseous phase(s) during hot-salt corrosion. Hot-
stage microscopy at temperatures above $750^{\circ}F$ showed corrosion
stains developing very rapidly over the specimen surface for a
short distance around salt crystals, but no liquid was actually
observed. The stains darkened very rapidly and appeared as a
solid corrosion product. It has not been established that the
mechanism of cracking requires a liquid phase, or that the me-
chanism changes at higher temperature. There was no evidence
of a liquid phase at temperatures below $700^{\circ}F$, and at tempera-
tures above $750^{\circ}F$ crack initiation was detected before the cor-
rosion stains were fully developed. An example of this is il-
lustrated in Figure 5, which shows several frames of a movie
taken at one frame per second during heating of a specimen to

800°F. Cracks were faintly visible after 14-1/2 minutes (Fig. 5b) and became clearly visible after 15 minutes (Figure 5c). Dark stains then developed around the cracks after 17 minutes (Figure 5d). The inflection in the incubation time-temperature curve may be due to melting at the salt-metal interface on a scale that cannot be resolved by hot-stage microscopy. Further work is needed to clarify this point.

Effect of Salt Composition on Crack Initiation

It was reported previously that different halide salts cause various degress of cracking in Ti-8Al-1Mo-1V at 650°F.[5] Therefore, the incubation time-temperature curve in Figure 4 is valid only for sodium chloride deposited on metallographically polished specimens of this alloy. A detailed study is now in progress to determine the effects of various salts on the cracking process, and complete results will be reported later. A few preliminary data, presented below, demonstrate that the type of salt has a strong influence.

Type of Salt	Salt Melting Point °F	Time to Initiate Cracking, mins.	
		450°F Exposure	475°F Exposure
NaCl	1470	No cracking after 11,220 minutes	5,760
CuCl	792	No cracking after 6,000 minutes	45
SnCl$_2$	475	1800	17

The melting points of these salts differ widely, but as yet there is no direct relationship between melting point and ability to promote cracking. Melting of the initial salt deposit should accelerate the stress corrosion process, as in the case of $SnCl_2$. However, salt melting does not appear to be essential for crack initiation. The possibility that the different salts have different amounts of retained moisture, or that they affect the amount of corrosion-produced hydrogen absorbed by the metal is being investigated.

The rate of crack propagation is also affected by the type of salt. In the case of $SnCl_2$, propagation is so rapid that hydrogen diffusion into the metal ahead of an advancing crack seems to be precluded as a mechanism for propagation. However, this does not preclude the possibility that propagation occurs by a stress-sorption mechanism, and that corrosion produced hydrogen is the sorbed species.

Effect of Alloy Composition on Crack Initiation

The time to initiate cracking by NaCl at $650^\circ F$ in four aluminum-bearing alloys increased with decreasing aluminum content, as shown in Figure 6. Ti-8Al-1Mo-1V was the most susceptible and cracked in 1-1/4 to 1-1/2 hours, whereas Ti-4Al-3Mo-1V cracked after 28 hours. Specimens of Ti-8Mn were not cracked after 48 hours exposure. Stressed specimens of Ti-8Mn were also exposed at $650^\circ F$ with $SnCl_2$ deposits, previously shown to be much more agressive than NaCl. Although no cracks were visible after 91 hours, specimens cracked during bending at room temperature after the salt was washed off, showing that corrosion embrittlement had occurred, Figure 7.

The susceptibility to cracking was not directly related to the extent of salt corrosion. Severe attack occurred on the Ti-8Mn and the Ti-4Al-3Mo-1V, which were the most resistant. This indicates that cracking probably is not caused by contact with a specific liquid or solid phase generated during corrosion. However, the degree of susceptibility to cracking in different alloys can be rationalized on the basis of various degrees of tolerance for hydrogen.

It was reported previously[5] that aluminum is preferentially attacked during hot-salt corrosion of Ti-8Al-1Mo-1V. The possible role of preferential attack of alloy and impurity elements in the stress corrosion mechanism is an area that requires further work.

CONCLUSIONS

Hot-salt cracking of titanium alloys occurs after an incubation period which is influenced by exposure temperature, salt composition, and alloy composition. The initiation of cracks is not related to the extent of salt corrosion which occurs, and therefore the cracking probably is not caused by contact with a specific liquid or solid phase in the corrosion products. Moisture seems to be the most critical ingredient in the corrosion process. This, coupled with the observation that cracks appear abruptly indicates that crack initiation occurs as a result of hydrogen embrittlement.

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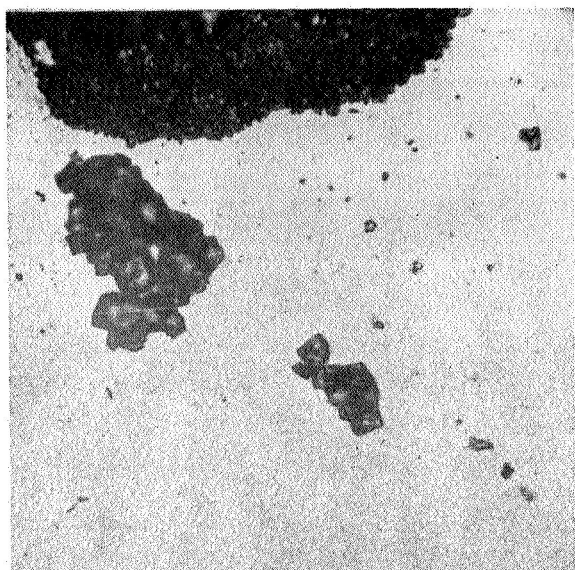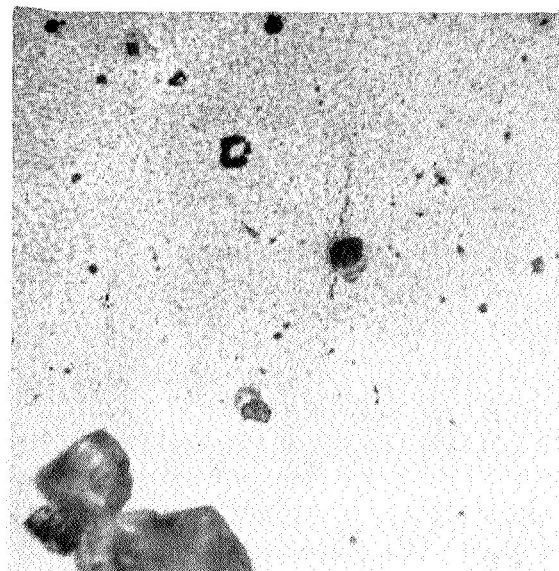
a. Salt deposit at room
    temperature (320X)
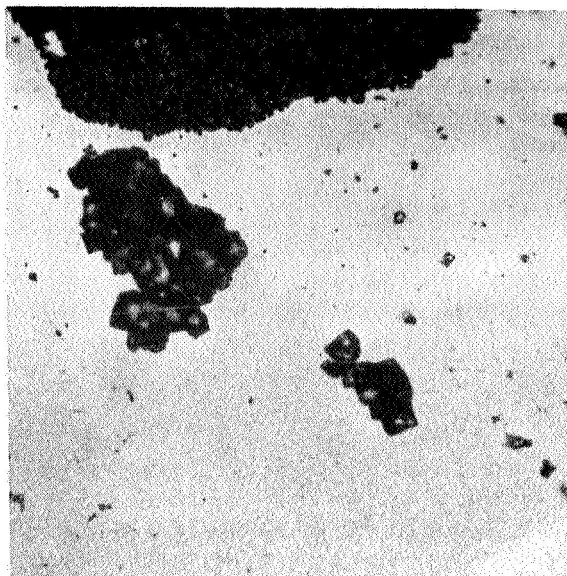
b. Same as (a) after reaching
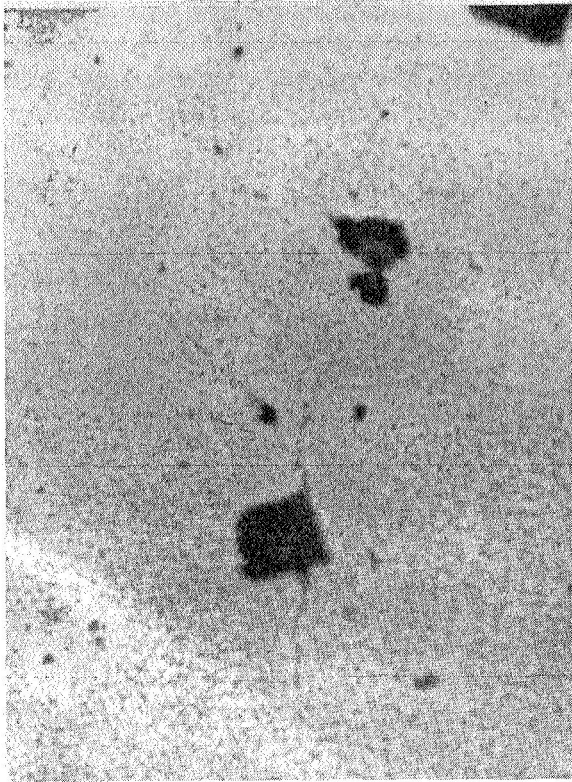   650°F (320X)
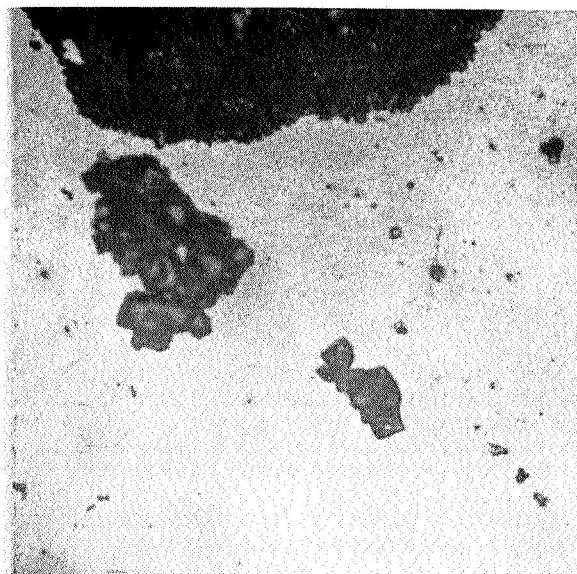
c. Same as (b) after 80 mm
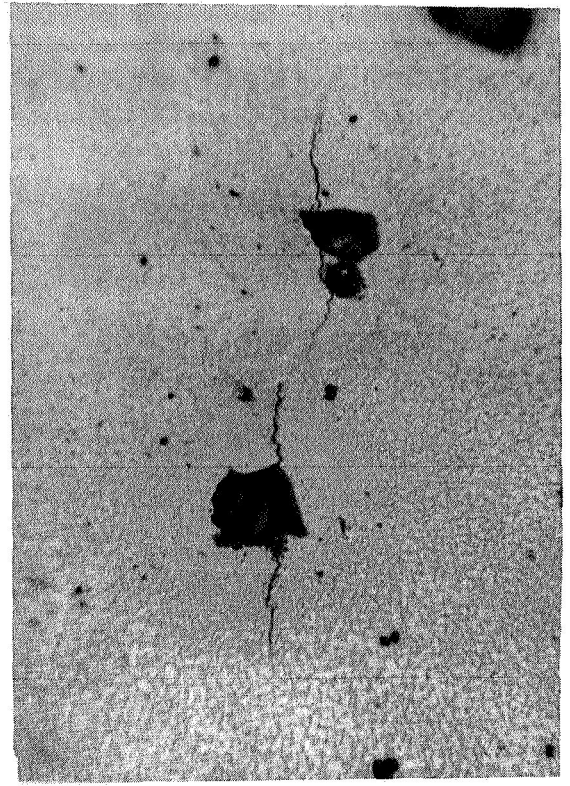   (320X)

d. Same as (c) enlarged to 800X

Figure 1. Hot-Stage Microscopy of NaCl Cracking of Ti-8Al-1Mo-1V
          at 650°F

a. 85 Minutes after reaching
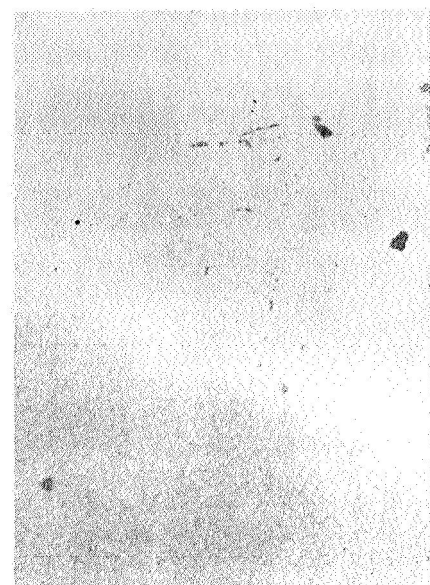   650°F

b. 185 Minutes after reaching
    650°F

Figure 2.   Hot-Stage Microscopy of NaCl Cracking of Ti-8Al-
            1Mo-1V at 650°F (720X)

a. Room temperature

b. Same as (a) after
    90 minutes at 650°F

c. Same as (b) after
    cooling to room
    temperature and
    removaloof salt
    crystal

Figure 3. Hot-Stage Microscopy of Ti-8Al-1Mo-1V Exposed to
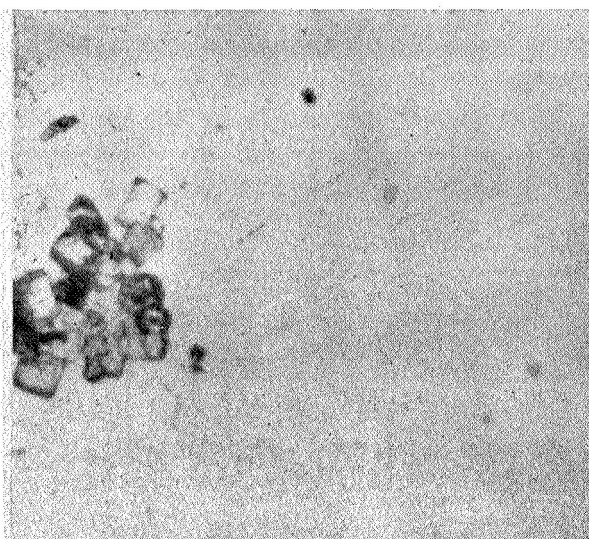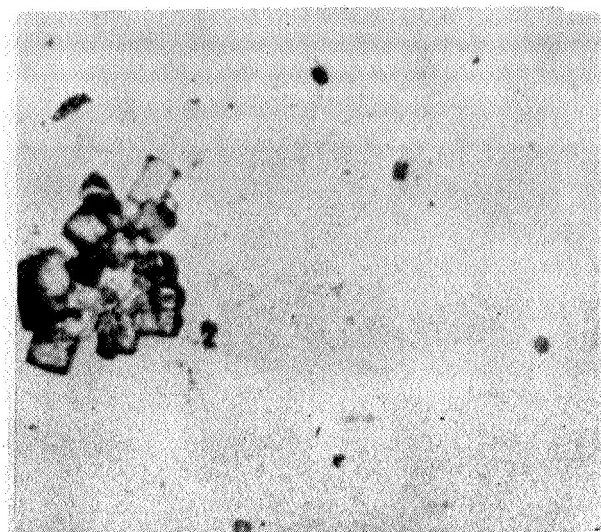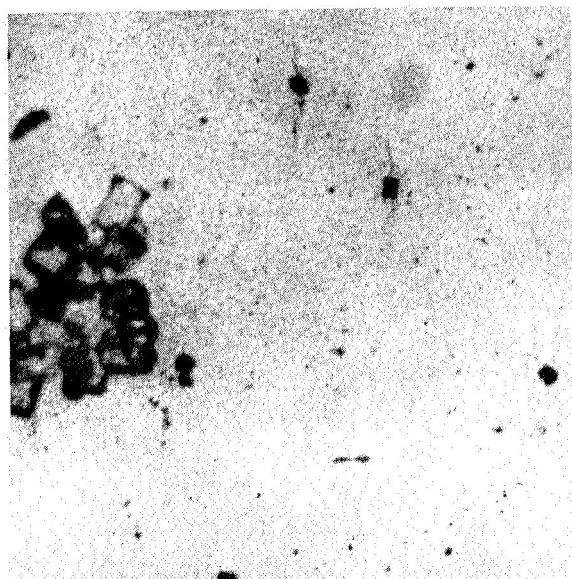   Pre-dried NaCl at 650°F (300X)
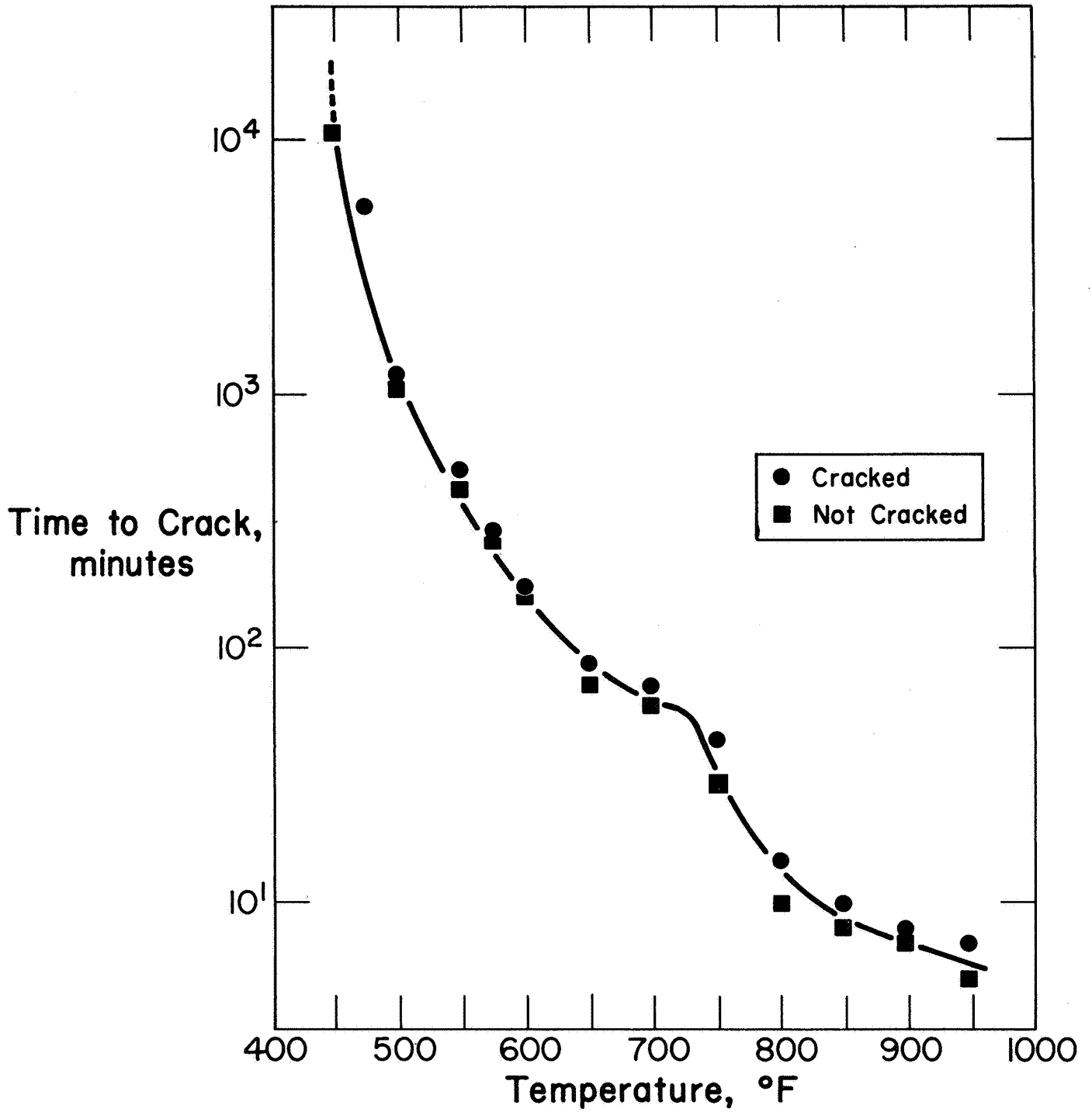
FIG. 4 TIME TO INITIATE CRACKING BY NaCl IN Ti-8Al-1Mo-1V vs TEMPERATURE
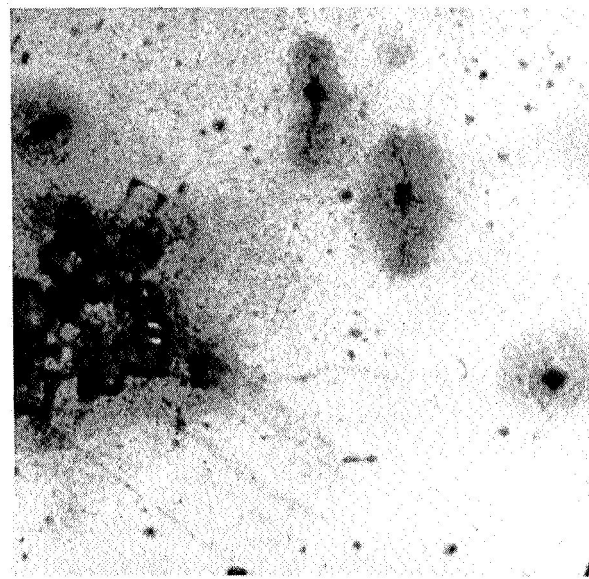
a. Salt deposit at room
    temperature

b. Same as (a) after 14.5 min-
    utes at temperature

c. Same as (a) after 15 min-
    utes

d. Same as (a) after 17
    minutes

Figure 5. Hot-Stage Microscopy of NaCl Cracking of Ti-
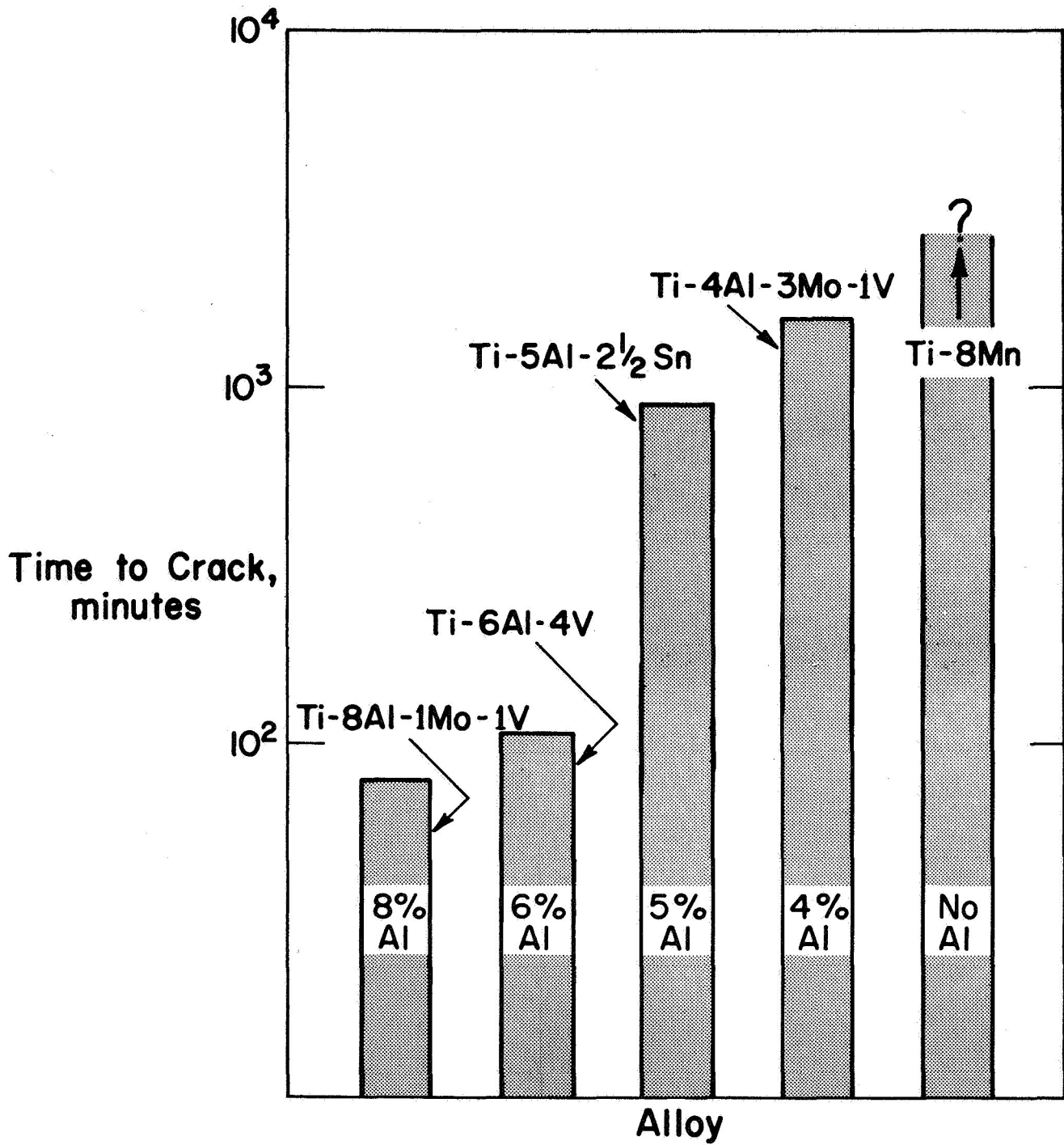   8Al-1Mo-1V at 800°F   (650X)

FIG. 6 EFFECT OF ALLOY COMPOSITION ON TIME TO INITIATE
CRACKING BY NaCl AT 650°F

Salt Exposed   Unexposed

FIGURE 7. Corrosion-Embrittlement of

Ti-8Mn Alloy (5X)

    Cracks were not visible after exposure of stressed specimen with SnCl$_2$ deposit at 650°F for 91 hours. Cracks were produced by bending the specimen at room temperature after the salt was washed off.